8-29-05

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

In re United States Patent Application of:	)	Docket No.:	4197-114
	)		
Applicant: Ralf-Uwe Bauer, et al.	)	Examiner:	Mark Osele
	)		
Application No.: 10/088,751	)	Confirmation No.:	8808
	)		
Date Filed: July 19, 2002	)	Art Unit:	1734
	)		
Title: METHOD FOR PRODUCING CELLULOSE SHAPED-BODIES	))))	Customer No.:	**23448**

EXPRESS MAIL CERTIFICATE

I hereby certify that I am mailing the attached documents to the Commissioner for Patents on the date specified, in an envelope addressed to the Mail Stop Appeal Brief-Patents, Commissioner for Patents, P. O. Box 1450, Alexandria, VA 22313-1450, and Express Mailed under the provisions of 37 CFR 1.10.

08/30/2005 SHASSEN1 00000004 10088751

01 FC:1402   500.00 OP

Candace White

August 26, 2005
Date

EO 005 704 749 US
Express Mail Label Number

BRIEF ON APPEAL IN U.S. PATENT APPLICATION NO. 10/088,751

Mail Stop Appeal Briefs-Patents
Commission for Patents
P. O. Box 1450
Alexandria, VA 22313-1450

Sir:

This Brief on Appeal is filed in support of the Notice of Appeal filed June 29, 2005 in U.S. Patent Application No. 10/088,751, appealing the decision of the Examiner in the April 1, 2005 Office Action, finally rejecting claims 1-17. Three copies of the Brief are enclosed. An oral hearing is not requested.

REAL PARTY IN INTEREST

The real party in interest in this appeal is Zimmer AG, the owner of the invention and patent rights of this application, by virtue of an Assignment of U.S. Patent Application No. 10/088,751 recorded in the assignment records of the U.S. Patent and Trademark Office on April 15, 2004 at reel 015212, frame 0930566 (5 pages).

RELATED APPEALS AND INTERFERENCES

There are no other appeals or interferences known to Appellant, the Appellant's legal representative, or assignee, which will directly effect or be directly affected by or have a bearing on the Board's decision in this appeal.

STATUS OF CLAIMS

Claims 1-17 are pending in the subject application and all claims 1-17 have been finally rejected in the April 1, 2005 Office Action. All the pending claims, that being claims 1-17, are being appealed herein. (A copy of appealed claims is in Appendix A)

STATUS OF AMENDMENTS

An Amendment After Final Rejection filed on May 26, 2005 was not entered. (See Advisory Action of June 20, 2005) However, no amendment of the pending claims was made in response to the Final Rejection of April 1, 2005, but the mere act of refusing entry did stop the inclusion of additional evidence presented by applicants.

SUMMARY OF CLAIMED SUBJECT MATTER

The present invention relates to a process of manufacturing cellulose mouldings have reduced cellulose decomposition when using TCF bleached or ECF bleached cellulose. The process involves dissolving a bleached cellulose pulp having a reduced number of carboxyl groups in an aqueous tertiary aminoxide to form a bleached solution, deforming the solution and coagulating this bleached solution to form the cellulose moulding. The Total Chloride-Free (TCF)-bleached cellulose comprises carboxyl group content in the range from 1 to 35 μmol/g and Elementary

Chloride-Free (ECF)-bleached cellulose comprising a carboxyl group content in the range from 1 to 50 μmol/g.

Thus, applicants' claimed invention comprises using a bleached cellulose pulp dissolved in an aqueous tertiary aminoxide solvent wherein the bleached cellulose has a reduced number of carboxyl groups and because of this reduced number of carboxyl groups there is reduced decomposition of the bleached cellulose with the additional benefits of increased polymerization and whiteness.

Claim No.	Features Recited by the Claim	Cross-Reference to the Specification
1.	A process for manufacture of cellulose mouldings with reduced cellulose decomposition from Total Chloride-Free (TCF) bleached or Elementary Chloride-Free (ECF) bleached cellulose, comprising: dissolving a bleached cellulose pulp having a reduced number of carboxyl groups in an aqueous tertiary aminoxide to form a bleached cellulose solution, wherein the reduced number of carboxyl groups causes reduced decomposition of the bleached cellulose in the process, and wherein the bleached cellulose is selected from the group consisting of: TCF-bleached cellulose comprising a carboxyl group content in the range from 1 to 35 μmol/g and ECF-bleached cellulose comprising a carboxyl group content in the range from 1 to 50 μmol/g; deforming the cellulose solution; and coagulating the deformed solution to generate a spinning solution for forming the cellulose moulding.	page 4, lines 1-5 page 4, line 10 page 4, line 12 page 6, lines 16-17
2.	The process according to claim 1, wherein the TCF-bleached cellulose comprises a carboxyl group content in the range from 15 to 30 umol/g.	page 4, line 29
3.	The process according to claim 1, wherein the ECF-bleached cellulose comprises a carboxyl group content in the range from 25 to 35 umol/g	page 4, line 30
4.	The process according to claim 1, wherein the N-methylmorpholin-N-oxide is used as the tertiary aminoxide.	page 5, line 2
5.	The process according to claim 1, further comprising introducing into the bleached cellulose solution at least one organic compound comprising at least four carbon atoms, at least two conjugated double bonds, and at least two substitutes -X-H,	page 5, lines 4-10

	whereby X has the significance of O or NR, and R is hydrogen or an alkyl group with 1 to 4 carbon atoms.	
6.	The process according to claim 1, wherein the decomposition of the cellulose is restricted to a fraction in the range from 3 to 20% by weight, related to the cellulose pulp used.	page 5, line 19
7.	A cellulose solution for the manufacture of mouldings comprising a TCF-bleach cellulose having a carboxyl group content in the range from 1 to 35μmol/g dissolved in a solvent containing a tertiary aminoxide.	page 4, lines 1-10
8.	A cellulose solution for the manufacture of mouldings comprising a ECF-bleached cellulose having a carboxyl group content in the range of 1 to 50μmol/g dissolved in a solvent containing a tertiary aminoxide.	page 4, lines 1-12
9.	The process according to claim 1, wherein the cellulose mouldings include a member selected from the group consisting of: fibres, filaments, and films.	page 1, line 3
10.	The process according to claim 1, wherein the cellulose mouldings formed from the bleached cellulose pulp having a lower content of carboxyl groups has a higher degree of whiteness relative to cellulose pulp having a higher content of carboxyl groups.	page 5, line 30 and page 7, lines 6-8
11.	The process according to claim 1, wherein the decomposition of the cellulose is restricted to a fraction in the range from 8 to 15% by weight, related to the cellulose pulp used.	page 5, line 20
12.	The process according to claim 1, wherein the cellulose solution comprises about 13% cellulose, about 10.5% water and about 76.5% of NMMO.	page 6, lines 14-15
13.	The process according to claim 1, wherein the cellulose mouldings formed from the bleached cellulose pulp having a lower content of carboxyl groups has a higher degree of polymerization relative to bleached cellulose pulp having a higher content of carboxyl groups.	page 7, lines 6-8
14.	The process according to claim 1, wherein the bleached cellulose pulp having a lower content of carboxyl groups has a lower degree of decomposition relative to bleached cellulose pulp having a higher content of carboxyl groups.	page 8, table 3
15.	A cellulose moulding article formed from a TCF-bleached cellulose according to claim 7.	page 4, lines 1-10
16.	A cellulose moulding article formed from a ECF-bleached cellulose according to claim 8.	page 4, lines 1-12
17.	The process according to claim 5, wherein the organic compound is isopropyl gallate.	page 5, line 16

GROUND OF REJECTION

Claims 1-17 were rejected under 35 U.S.C. §103(a) as being unpatentable over XP-002161407 (Rogowin S. A.). The only issue is whether the subject matter recited in claims 1-17 is obvious in light of the XP-002161407 (Rogowin S. A.) reference.

CITED REFERENCE

XP-002161407 (Rogowin S. A.) 1960. A copy of the Rogowin German reference is included in the Evidence Appendix . Also include in the Evidence Appendix is a translation of the Rogowin reference evidence submitted by applicants on December 28, 2004.

GROUPING OF CLAIMS

Group I: Claims 1-6, 9-14 and 17 constitute a unitary group of claims presenting common issues in respect of their patentability. Claim 1 is representative of the group.

Group II: Claim 7, 8, 15 and 16 constitute a unitary group of claims presenting common issues in respect of their patentability. Claim 7 is representative of the group.

ISSUE

The only issue that must be determined by this Board is whether the reference Rogowin discloses, teaches or suggests all claimed elements of claims 1-17.

ARGUMENT

Group I including claims 1-6, 9-14 and 17, claim 1 is representative

For the Office to establish a *prima facie* case of obviousness, three basic criteria must be met. First, there must be some suggestion or motivation, either in the reference itself or in the knowledge generally available to one skilled in the art, to modify the reference. Second, there must be a reasonable expectation of success. Finally, the prior art reference must teach or suggest

all the claim limitations. The Rogowin reference does not meet this standard.

As set forth above, applicants' claimed invention comprises a bleached cellulose pulp dissolved in an aqueous tertiary aminoxide solvent wherein the bleached cellulose has a reduced number of carboxyl groups and because of this reduced number of carboxyl groups there is reduced decomposition of the bleached cellulose and increased polymerization and whiteness in the final lyocell product.

The Office has cited a reference that was published in 1960 and relates to the use of cellulose for the production of viscose fibres. Thus, this reference discusses production of an artificial fiber that was available nearly thirty years before the lyocell process or lyocell fiber of the present invention. As will be shown by applicants, hereinbelow, it is well known in the textile industry that viscose and lyocell are entirely different products, produced with entirely different methods, and with entirely different physical properties.
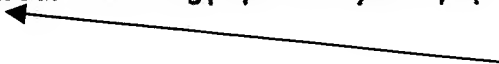
According to the Office:

> "A person of ordinary skill addressing the problem of reducing cellulose decomposition would directly deduce from Rogowin S.A. that the carboxyl group content of cellulose must be as low as possible. It would have been obvious to one of ordinary skill in the art that this could be accomplished by either blocking the carboxyl groups as shown by Rogowin S.A. or keeping the carboxyl content as low as possible in the starting material. It progresses therefrom that decomposition will be lower when the carboxyl group content is low."

The first criteria to prove obviousness is satisfied if the Office can show that the Rogowin reference provides some suggestion or motivation to stop blocking the carboxyl groups with calcium, and instead, reduce the number of carboxyl groups.

Applicants admit that the Rogowin reference states in the first sentence of the third paragraph that "[t]he carboxyl groups decrease the thermostability of cellulose and the fibers made thereof." However, that is all the reference states and it certainly provides no teaching or suggestion of reducing the content of carboxyl groups. Instead, the Rogowin reference goes to great lengths to show that the only way to solve this problem is to block the carboxyl groups with a calcium ion. Specifically, the reference discusses in the last sentence of Section 7.314

that to increase light resistance and thermostability (related to decomposition) of the fibres, the carboxyl groups **have to be blocked**, as shown below.

Consequently, to obtain an increase of the light resistance and thermostability of the obtained fibres, the carboxyl groups have to be blocked in the starting pulp or the hydrate-pulp.

Notice that this is not a hedging statement and does not use the word "may" but instead states emphatically that the carboxyl groups **have** to be blocked. Applicants question, after reading the Rogowin reference, why a skilled artisan would even consider foregoing the blocking of the carboxyl groups with calcium ions, but instead, reduce the amount of carboxyl groups? One skilled in the art would certainly review the results set forth in Table 33 of Rogowin, recreated below for ease of discussion, and determine that a small number of carboxyl groups was detrimental to the final product.

Cellulose	Content of COOH-groups of the cellulose [%]	Decrease of the polymerization degree after heating based on the primary polymerization degree [%]
Breech tree pulp I	0.004	24.8
Beech tree pulp II	0.046	4.9
Pine tree pulp I	0.004	28.3
Pine tree pulp II	0.1	4.8

The test results set forth in Table 33 of Rogowin do not show that reducing the carboxyl groups provides any benefits or is an acceptable alternative. Instead, the results show that a cellulose sample with a reduced number of carboxyl groups (0.004 %) has a 25% reduction in polymerization. However, a cellulose sample with an increased number of carboxyl groups (0.046% or 0.1%) but **blocked with calcium** shows only a 4% reduction in polymerization. Thus, one skilled in the art would certainly understand that blocking the carboxyl groups is far more effective then reducing the number of carboxyl groups. What is the motivation put forth in the cited reference to lower the carboxyl count when the results show that a cellulose with a lower carboxyl count exhibited reduced polymerization when compared to blocking the carboxyl groups with a calcium cation? Clearly, this is none.

Further, the Rogowin reference discusses at the top of page 169 that

As shown by the data of the Table small amounts of COOH-groups cause the degregation of cellulose by heating. By blocking said groups the intensity of said thermal degregation is substantially decreased.

Thus, Rogowin teaches that even a small amount of carboxyl groups causes the degradation of the cellulose during heating. The only solution that Rogowin provides relates to blocking the carboxyl groups with calcium ions, and only then, the intensity of the thermal degradation is substantially decreased. The results in Table 33 show that even with an increase in carboxyl groups, there is reduced degradation if these carboxyl groups are blocked.

Accordingly, if Rogowin states that calcium blocking is essential, where is there any motivation to bypass this blocking and instead reduce the number of carboxyl groups? As stated above, there is none. Thus, it is very clear that this reference provides no incentive to reduce the carboxyl groups. Accordingly, the Rogowin reference does not meet the first requirement for establishing a *prima facie* case of obviousness, that being, motivation to modify the reference.

The second criterion that must be met to establish a *prima facie* case of obviousness includes some reasonable expectation of success when modifying Rogowin by reducing the number of carboxyl groups, instead of just blocking the carboxyl groups with calcium as preferred by Rogowin. Although this argument is redundant, the results in Table 33 are not very promising for any modification relating to reducing the number of carboxyl groups because when the number of carboxyl groups is low (0.004%) there is a large reduction in polymerization. Certainly, polymerization is important, and as such, applicants doubt that one skilled in the art reading this reference would be willing to give up polymerization by reducing carboxyl groups.

Further, there is the statement at the top of page 169, as discussed above, which provides incentive to block the carboxyl groups to substantially decrease thermal degradation, especially in light of the fact that a smaller number of carboxyl groups caused degradation, as stated by Rogowin.

Notably, Rogowin further discusses another problem with bleached cellulose, that being the formation of aldehydes $R-C{\overset{H}{=}}O$, in addition to that of carboxyl groups $R-{\overset{O}{\underset{}{C}}}-O$, and these aldehyde groups have an important influence with respect to alkaline resistance and thermo resistance of the cellulose. **Rogowin states that as the number of aldehyde groups increases, the resistance of cellulose against alkalines is reduced and the cellulose will be more**

intensively decomposed by the treatment with alkalines. Further, these aldehyde groups effect the discoloration of cellulose at higher temperatures. With these negative effects due to the aldehydes, one would be very concerned about introducing the cellulose into a strong alkaline solution. Instead, Rogowin teaches that the introduction of cellulose into water (with a pH of about 7) seems to address the problems of both the carboxyl groups and aldehyde groups. Specifically, the calcium in the water binds with the carboxyl groups, thereby blocking the carboxyl groups, and also, water with a neutral pH does not decompose the material.

Interestingly, applicants do the exact opposite of that taught in Rogowin, they reduce the number of carboxyl groups and dissolve the cellulose in a strong alkaline solution. Clearly, the Rogowin reference provides no expectation of success when going in the direction of applicants' claimed invention. However, the Office contends that:

> "Although Rogowin teaches that calcium blocking of carboxyl groups can decrease the amount of depolymerization, it does not eliminate the depolymerization completely. Elimination of carboxyl groups in the first place would achieve results at least as good as calcium blocking, if not better. Furthermore, elimination of carboxyl groups **in the base material** would eliminate the need for calcium blocking, which may not be feasible for all process." (emphasis added)

This statement by the Office is speculative at best because after a thorough review of Rogowin there is no statement made in the reference to reduce the carboxyl groups that provides any positive result. However, as stated above, the Rogowin reference expressly states that the carboxyl groups do decrease the thermostability of cellulose but then shows by the results in table 33 that reducing the number of carboxyl groups is not effective. Instead, the carboxyl groups **have to be blocked in the starting material.** This concept is in direct conflict with the contention of the Office that states "elimination of carboxyl groups **in the base material** would eliminate the need for calcium blocking, which may not be feasible for all process."

Interestingly, the statement made in Rogowin regarding the importance of calcium blocking in combination with the aldehyde discussion relating to the detrimental effects of aldehyde groups in the presence of alkaline, provides evidence that the reference teaches away from going in the direction of applicants' claimed invention.

According to the Office, because Rogowin teaches that bleached cellulose exhibits discoloration and decomposition at high temperatures due to the presence of carboxyl groups, that this problem is present regardless what type of bleached cellulose is used or whether a particular solvent is

9

possibly decomposed with the cellulose (see page 2 of April 1, 2005 OA). However, this contention is not supported by the reference but merely by the Office's speculation. Rogowin recognizes that carboxyl groups and aldehyde groups are problematic and to rectify the problems, the carboxyl groups are blocked and an alkaline solution is avoided to overcome the problems related to the aldehyde groups.

Importantly, applicants have gone in the opposite direction from the teachings of Rogowin. Firstly, applicants dissolve the base material in a highly alkali environment, this is in spite of the statement in Rogowin that cellulose is decomposed by the treatment of alkalines and that aldehydes effect discoloration of cellulose. Clearly, the lyocell process is so different from that of the viscose process, discussed in this 1960 Rogowin reference, that treatment of cellulose in the highly alkali environment such as N-methylmorpholin-N-oxide (NMMO) does not have a deleterious effect on the lyocell fiber. NMMO is a relatively strong oxidizing agent and used as an oxidizing agent in organic synthesis. Interestingly, NMMO oxidizes reducing ends in cellulose chains to aldehydes $\overset{H}{\underset{O}{R-C=O}}$ or carboxylic acids $\overset{O}{R-C-O}$ but also generates new keto $\overset{O}{R-C-R}$ structures along the chain by random oxidation of hydroxyl groups. Thus, by the mere process of mixing the NMMO with the cellulose, there is an increase in the production of carbonyl groups. Notably, an increase in aldehydes, is something that Rogowin is attempting to avoid by not contacting cellulose with a strong alkaline.

According to the Office, one skilled in the art would not consider there to be any difference between lyocell and viscose. Applicants vigorously contest this conclusion. Clearly, at the time of the Rogowin reference, written many years before the discovery of lyocell, there was no indication that characteristics and/or properties of viscose could be transferred to all known or yet undiscovered cellulose products. Woodings in 1995 (Evidence Appendix) discussed the differences between the newly discovered lyocell relative to viscose. Specifically, at page 306, column 2, Woodings discussed that lyocell and viscose were so different that lyocell deserved a separate marketing strategies. Further, it is stated that lyocell as a "1.5 denier fibre, it could be spun into yarns with a better strength conversion factor than other cellulosic fibres, allowing rotor-spun lyocell to out-perform ringspun cotton or modal viscose." Woodings, provided specifics of the different characteristics of the fibers as set forth in Table 1, recreated below.

Table 1 The properties of selected commercial rayon fibres

Property	Cuprammonium	Regular rayon	Improved rayon	Modal	Polynosic	'Y'-shaped rayon*	Solvent-spun rayon†
Fibre cross-section							
Dry tenacity (cN/tex)	15-20	20-24	24-30	34-36	40-45	18-22	40-44
Extensibility at break % (dry)	7-23	20-25	20-25	13-15	8-12	17-22	14-16
Wet tenacity (cN/tex)	9-12	10-15	12-16	19-21	30-40	9-12	34-38
Extensibility at break % (wet)	16-43	25-30	25-35	13-15	10-15	23-30	16-18
Water imbibition (%)	100	90-100	90-100	75-80	55-70	100-110	65-70
Cellulose D.P.	450-550	250-350	250-350	300-500	550-700	250-350	550-600
Initial wet modulus (@ 5%)	30-50	40-50	40-50	100-120	140-180	35-45	250-270

*The 'Y'-shaped rayon data are based on Courtaulds' Galaxy fibre
†The solvent-spun rayon data are based on Courtaulds' Tencel fibre

Clearly, the tenacity of lyocell compared to viscose is very different, whether in a wet or dry mode, and importantly, lyocell exhibits much higher strength in both wet and dry mode. The difference in the initial wet modulus is very significant because it is an indication of the strength of the fibers and the degree of tenacity required to produce an elongation of 5% when the specimen is completely wet. Additionally, the lyocell is a much stronger fiber because of the required stress to stretch the fiber. The cross-sections of the fibers are also different wherein the viscose is serrated and the lyocell is circular. Further, Woodings states that

> The lyocell fibres now being introduced have the capability to halt the overall decline in manmade cellulosic fibres' share of the world market. In clothing textiles, Courtaulds' Tencel™ had early successes in market sectors which were previously closed to the other manmade cellulosic fibres. The combination of the unique fibre properties with novel fabric and garment finishing techniques yielded highly desirable garment aesthetics. These aesthetics have proved attractive in garments as diverse as denim and underwear.
>
> In non-woven fabrics, lyocell's inherent strength and 'bondability' have led to a variety of new applications which were not possible with viscose rayon. In hydro-entanglement, one of the fastest growing sectors of the non-woven industry, the use of Courtaulds' lyocell is now showing several advantages over other cellulosic fibres. Compared with viscose or cotton, it allows the manufacture of a wider range of basis weights, with higher strengths, better appearance and improved dry and wet textures. At high bonding pressures, it has enabled the production of non-woven fabrics which are stronger than the same weight of woven cotton. When fibrillated by refining or very-high-pressure hydroentanglement, the microfibres generated may be used in leather- or suede-like materials, efficient filters, or even durable papers.

unique fiber properties

Comparison with Viscose

A more recent article by Colom (2002) (copy in Evidence Appendix) clearly sets forth the differences between viscose and lyocell. As stated at page 2229, column 2, "[i]t has been observed that during the mercerisation treatment the viscose type fibres are more affected to the degradation caused by the transformation of crystalline cellulose II to amorphous cellulose, <u>to the point of total dissolution at high caustic concentrations for modal and viscose</u>. For lyocell fibres, this transformation is partial and d<u>issolution at high concentrations does not occur. This can be explained by the orientation and high crystallinity of the lyocell macromolecules</u>." Thus, it is evident that viscose fibers experience complete dissolution at high caustic concentration while for lyocell there is no dissolution. This reference from 2002 discusses facts that applicants discovered when they invented the presently claimed invention previously to the 2002 reference. Of course, this would not be known from the Rogowin reference because Lyocell was not even thought of in 1960.

One skilled in the art, at the time this present invention was discovered, already knew that there were major differences between the viscose product and process of making same relative to the lyocell product and process of making same, even though they both use cellulose as starting material, evidenced by the Woodings article of 1995. Thus, one skilled in the art, at the time of filing of the present invention, would not look to the Rogowin reference for any guidance relating to the lyocell product or process of making same. Notably, Applicants had introduced additional evidence relating to this matter, but because the Office would not enter the Response to Final Rejection filed on May 26, 2005, even though applicants had not amended the claims, the evidence submitted with that response could not be included in this brief.

Lastly, the cited reference does not disclose each and every element of applicants' claimed invention. Initially, where in the Rogowin reference is there any suggestion for using a cellulose material with a reduced number of carboxyl groups in an **aqueous tertiary monoxide,** such as NMMO? Unmistakably, there is no mention of taking such cellulose and dissolving it in NMMO in the Rogowin reference. Instead as stated above, Rogowin teaches away from the use of a strong alkaline solution due to the problems related to decomposing of the cellulose by the treatment of alkalines

Further, where is there any teaching or suggestion to reduce the carboxyl groups. Applicants have reviewed the Rogowin reference and nowhere in this document is there any expressed statement that states that there should be a reduction in carboxyl groups. Instead, the reference

only discusses blocking the carboxyl groups. Blocking and eliminating are two completely different actions. The translation states "carboxyl groups decrease thermostability of the cellulose but then immediately describes the need for blocking the carboxyl groups.

The following table clearly defines the specifics of the cited reference and shows the differences between the presently claimed invention and that of Rogowin.

	Fiber	Disclosed Effects of Blocking of Carboxyl Groups	Disclosed Effects of Reduction of Carboxyl Groups	Disclosed Effects of Dissolving in Alkaline
Prior Art Rogowin	Viscose	**Positive effects** caused an increase in polymerization (Table 33); caused an increase in thermostability and light resistance (last paragraph of section 7.314)	**Positive effect** None stated	**Positive effect** None stated
		Negative effects None stated	**Negative effect** decrease of polymerization (Table 33); small amount of COOH groups caused the degradation of cellulose by heating (first sentence in second paragraph on page 169)	**Negative effect** detrimental to solution due to the presence of aldehydes, that caused the composition to decompose in alkaline (second paragraph in section 7.314)
Present Invention	Lyocell	**Positive effect** NA	**Positive effect** reduced decomposition; caused an increase in polymerization and whiteness	**Positive Effect** required for production of lyocell fibers of the present invention
		Negative effect NA	**Negative effect** None stated	**Negative effect** None stated

In light of the above discussion and the fact that (1) there is no motivation, suggestion or teaching to modify the reference; (2) there is no expectation of success by modifying the process in the reference and (3) each and every recited limitation of applicants' claimed invention is not disclosed or suggested in the cited reference, it is clear that the cited reference fails to establish a *prima facie* case of obviousness of applicants' claimed invention.

According, applicants request that the Board take cognizance of the absence of proper basis of the §103 rejection of claims 1-6, 9-14 and 17 and correspondingly reverse the Office's rejection of such claims.

Group II includes claims 7, 8, 15 and 16 and claim 7 is representative

13

Claim 7 is representative and recites:

> 7.   A cellulose solution for the manufacture of mouldings comprising a TCF-bleach cellulose having a carboxyl group content in the range from 1 to 35$u$mol/g dissolved in a solvent containing a tertiary aminoxide.

This claim requires a cellulose solution of a bleached cellulose having a low carboxyl group content and dissolved in a tertiary aminoxide. A tertiary aminoxide is an alkaline compound, and Rogowin clearly teaches away from dissolving a cellulose material in an alkaline solution due to the problems associated with decomposition caused by the aldehyde. Considering the problems of decomposition caused by an alkaline solution, applicants suggest that the cited reference teaches away from applicants' claimed invention. The Court in *In re Gurley*, 31 USPQ2d 1131 (Fed. Cir. 1994) addressed this very issue and stated:

> "[I]n general, a reference will teach away if it suggest that the line of development flowing from the reference's disclosure is unlikely to be productive of the result sought by the applicant. See United States v. Adams, 383 U.S. 39, 52, 148 USPQ 479, 484 (1966) ("known disadvantages in old devices which would naturally discourage the search for new inventions may be taken into account for determining obviousness.)"

Surely, anyone skilled in the art reading the Rogowin reference would be discouraged from going in the direction that applicants have gone.

The Office stated in the Advisory Action of June 20, 2005:

> "Applicants' arguments are directed to alleged shortcomings if one in the art were to follow the motivation of Rogowin for performing the instantly claimed method. Some manufactures may have different priorities for end products. When a high degree of polymerization is not crucial, a starting material with a low carboxyl content could be preferable."

Applicants find this statement breathtaking. So, even though there are numerous shortcomings in the Rogowin reference, and it does not teach any information relating to the lyocell product or process, the Office contends that one would use this reference as a starting point and perhaps serendipitously a successful product may be produced. Applicants argue that this statement by the Office amounts to the application of an "obvious to try" standard which is known to be an improper standard for a §103 rejection. This very issue was addressed by the Board of Patent

Appeals and Interferences in *Ex parte Goldgaber*, 41 USPQ2d 1172 (B.P.A.I. 1996) (quoting *In re Eli Lilly and Co.*, 14 USPQ2d 1741, 1743 (Fed. Cir. 1990)) and the Board stated that "an 'obvious-to-try' situation exists when a general disclosure may pique the scientist's curiosity, such that further investigation might be done as a result of the disclosure, but the disclosure itself **does not** contain a sufficient teaching of how to obtain the desired result, **or that the claimed result would be obtained if certain directions were pursued."** (emphasis added).

Once again, it is clear that the cited reference fails to establish a *prima facie* case of obviousness of applicants' claimed invention. It therefore is respectfully requested that the Board take cognizance of the absence of proper basis of the §103 rejection of claims 7, 8, 15 and 16 and correspondingly reverse the Office's rejection of such claims.

CONCLUSION

Based on the foregoing arguments and cited legal precedent, it is respectfully requested that the Board of Patent Appeals and Interferences reverse the decision of the Office finally rejecting claims 1-17 now pending in the application, consistent with the patentability of such claims over the cited art reference.

Enclosed with this appeal brief is a Credit Card Payment form, authorizing the Office to charge the entry fee in the amount of $500.00 under 37 C.F.R. §1.17(c) to the credit card specified therein. Please charge any deficiency and credit any excess payment to Deposit Account No. 08-3284 of Intellectual Property/Technology Law.

Respectfully submitted,

Marianne Fuierer
Reg. No. 39,983
Attorney for Applicants

INTELLECTUAL PROPERTY/
TECHNOLOGY LAW
P. O. Box 14329
Research Triangle Park, NC 27709
Phone: (919) 419-9350
Fax: (919) 419-9354
Attorney File: 4197-114

CLAIM APPENDIX

Pending and Appealed Claims 1-17

1.   (Previously presented) A process for manufacture of cellulose mouldings with reduced cellulose decomposition from Total Chloride-Free (TCF) bleached or Elementary Chloride-Free (ECF) bleached cellulose, comprising:

dissolving a bleached cellulose pulp having a reduced number of carboxyl groups in an aqueous tertiary aminoxide to form a bleached cellulose solution, wherein the reduced number of carboxyl groups causes reduced decomposition of the bleached cellulose in the process, and wherein the bleached cellulose is selected from the group consisting of: TCF-bleached cellulose comprising a carboxyl group content in the range from 1 to 35 μmol/g and ECF-bleached cellulose comprising a carboxyl group content in the range from 1 to 50 μmol/g;

deforming the cellulose solution; and

coagulating the deformed solution to generate a spinning solution for forming the cellulose moulding.

2.   (Previously presented) The process according to claim 1, wherein the TCF-bleached cellulose comprises a carboxyl group content in the range from 15 to 30 umol/g.

3.   (Previously presented) The process according to claim 1, wherein the ECF-bleached cellulose comprises a carboxyl group content in the range from 25 to 35 umol/g.

4.   (Previously presented) The process according to claim 1, wherein of N-methylmorpholin-N-oxide is used as the tertiary aminoxide.

5.   (Previously presented) The process according to claim 1, further comprising introducing into the bleached cellulose solution at least one organic compound comprising at least four carbon atoms, at least two conjugated double bonds, and at least two substitutes -X-H, whereby X has the significance of O or NR, and R is hydrogen or an alkyl group with 1 to 4 carbon atoms.

6.   (Previously presented) The process according to claim 1 wherein the decomposition of the cellulose is restricted to a fraction in the range from 3 to 20% by weight, related to the cellulose pulp used.

7.	(Previously presented) A cellulose solution for the manufacture of mouldings comprising a TCF-bleach cellulose having a carboxyl group content in the range from 1 to 35μmol/g dissolved in a solvent containing a tertiary aminoxide.

8.	(Previously presented) A cellulose solution for the manufacture of mouldings comprising a ECF-bleached cellulose having a carboxyl group content in the range of 1 to 50μmol/g dissolved in a solvent containing a tertiary aminoxide.

9.	(Previously presented) The process according to claim 1, wherein the cellulose mouldings include a member selected from the group consisting of: fibres, filaments, and films.

10.	(Previously presented) The process according to claim 1, wherein the cellulose mouldings formed from the bleached cellulose pulp having a lower content of carboxyl groups has a higher degree of whiteness relative to cellulose pulp having a higher content of carboxyl groups.

11.	(Previously presented) The process according to claim 1, wherein the decomposition of the cellulose is restricted to a fraction in the range from 8 to 15% by weight, related to the cellulose pulp used.

12.	(Previously presented) The process according to claim 1, wherein the cellulose solution comprises about 13% cellulose, about 10.5% water and about 76.5% of NMMO.

13.	(Previously presented) The process according to claim 1, wherein the cellulose mouldings formed from the bleached cellulose pulp having a lower content of carboxyl groups has a higher degree of polymerization relative to bleached cellulose pulp having a higher content of carboxyl groups.

14.	(Previously presented) The process according to claim 1, wherein the bleached cellulose pulp having a lower content of carboxyl groups has a lower degree of decomposition relative to bleached cellulose pulp having a higher content of carboxyl groups.

15.	(Previously presented) A cellulose moulding article formed from a TCF-bleached cellulose according to claim 7.

16.   (Previously presented) A cellulose moulding article formed from a TCF-bleached cellulose according to claim 8.

17.   (Previously presented) The process according to claim 5, wherein the organic compound is isopropyl gallate.

EVIDENCE APPENDIX

Cited Reference:

Rogowin S.A., "Chemiefasern," VEB Fachbuchverlag, Leipzig, 1960, XP-002161407, pages 168-169.

Translation of Rogowin reference was submitted by applicants on December 28, 2004 and accepted by the Office by reference in the April 1, 2005 Office Action.

Publication included herewith were also submitted on December 28, 2004 and accepted by the Office by reference thereto in the April 1, 2005 Office Action.

Woodings, C. R., (1995) The development of advance cellulosic fibres, *Int J. Biol. Macromol.*, V. 17 (6), p 305-309.

Colom, et al., (2002) Cystallinity changes in lyocell and viscose-type fibres by caustic treatment, *European Polymer Journal*, V. 38, p 2225-2230.

XP-002161407

Pentosane-, Mannose-. und Xylosereste können zusammen mit Zelluloseresten als gemischte. Zellulosekette vorliegen, oder es sind neben den Makromolekülen der Zellulose auch noch Makromoleküle anderer Hexosane und Pentosane vorhanden. Deshalb ist es zweckmäßig, bei der Bestimmung der Pentosane folgendes zu berücksichtigen: a) den Gesamtgehalt an Pentosanen im Zellstoff; b) die Pentosanmenge, die durch Behandlung mit 18%iger Natronlauge nicht entfernt wird.

Man hat Untersuchungen über die Änderung des Mannan- und Xylangehalts in Sulfitzellstoff während der einzelnen Stadien des technologischen Herstellungsprozesses von Viskoseseide durchgeführt [13]. Dabei ergab sich, daß 1 bis 3% Mannan und 2 bis 4% Xylan (bezogen auf Zellulose) fest mit der Zellulose verbunden sind und in der Viskosefaser verbleiben.

Zu einer genaueren Charakteristik der Zellstoffqualität ist es zweckmäßig, den Gehalt der verschiedenen Polysaccharide zu bestimmen. Dabei handelt es sich insbesondere um Mannan, Xylan und Polyuronsäuren, die einen bestimmten Einfluß auf die Löslichkeit der erhaltenen Zelluloseester sowie auf die Filtrierbarkeit der Spinnlösungen ausüben können.

7.314 *Die Aldehyd- und Karboxylgruppen*

Als Folge von oxydativen Nebenreaktionen, die bei der Zellstoffbleiche ablaufen, können im Zellulosemakromolekül neben den Hydroxylgruppen auch Aldehyd- und Karboxylgruppen auftreten. Das Vorkommen von Karboxylgruppen läßt sich auch durch die Bildung von gemischten Makromolekülen, die Uronsäurereste enthalten, während der biochemischen Synthese erklären.

Die im Zellulosemolekül gebildeten Aldehydgruppen werden mit Hilfe der Kupfer- oder Jodzahl bestimmt und zeigen einen wesentlichen Einfluß auf die Alkali- und Thermoresistenz der Zellulose. Je höher der Gehalt an Aldehydgruppen ist, um so geringer ist die Beständigkeit der Zellulose gegen Alkalien und um so intensiver wird die Zellulose bei der Behandlung mit Alkalien abgebaut, insbesondere bei der Merzerisierung. Ferner beeinflussen die Aldehydgruppen auch die Verfärbung der Zellulose bei höherer Temperatur [14]. Je größer die Zahl der Aldehydgruppen ist, um so stärker vergilbt die Zellulose bei höheren Temperaturen (40 bis 60 min lang bei 110 °C).

Die Karboxylgruppen setzen die Thermostabilität der Zellulose und der aus ihr erhaltenen Fasern herab. Tabelle 33 enthält Angaben [15] über die Änderung des Poly-

Tabelle 33. Einfluß des Karboxylgruppengehalts in Zellstoff auf den Polymerisationsgrad der Zellulose nach Erhitzen

Zellstoff	Gehalt an COOH-Gruppen, bezogen auf den Zellstoff [%]	Verringerung des Polymerisationsgrades nach Erhitzen, bezogen auf den ursprünglichen Polymerisationsgrad [%]
Buchenzellstoff I	0,004	24,8
Buchenzellstoff II	0,046	4,9
Kiefernzellstoff I	0,004	28,3
Kiefernzellstoff II	0,1	4,8

merisationsgrades von Zellstoffen mit geringem Karboxylgehalt (0,004 bis 0,1 %) nach einstündiger Erhitzung auf 105 °C. Bei den mit II bezeichneten Proben sind die freien Karboxylgruppen durch Waschen mit hartem Wasser mittels Calciums blockiert..

Wie aus den Angaben der Tabelle hervorgeht, verursachen selbst geringe Mengen an COOH-Gruppen einen Abbau der Zellulose beim Erwärmen. Durch eine Blockierung dieser Gruppen wird die Intensität des thermischen Abbaues wesentlich verringert. Der Einfluß der Karboxylgruppen äußert sich auch darin, daß die Lichtbeständigkeit der Zellulose und der aus ihr erhaltenen Fasern verringert wird. So färben sich z.B. eine ungebleichte Viskosestapelfaser, bei der 1 COOH-Gruppe auf 500 bis 550 Elementarglieder kommt, und eine mit H_2O_2 (1,5 g/l) gebleichte Probe, bei der 1 COOH-Gruppe auf 300 bis 370 Glieder kommt, bei längerer Trocknung merklich gelb.

Folglich müssen zur Erhöhung der Licht- und Wärmebeständigkeit der erhaltenen Faser die im Ausgangszellstoff oder in der Hydratzellulose vorhandenen Karboxylgruppen blockiert werden.

7.315   Das Lignin

Die quantitative Bestimmung des Lignins nach den verschiedenen Methoden ergibt keine übereinstimmenden Werte. Die Mehrzahl der vorgeschlagenen Methoden zur Ligninbestimmung beruhen darauf, daß die Zellulose und die anderen Polysaccharide mit Hilfe von konzentrierten Mineralsäuren vollständig hydrolysiert und aufgelöst werden. Der Rückstand enthält alle durch Säuren nicht hydrolysierbaren Stoffe, d.h. das Lignin, die Fette und Harze sowie einen Teil der Asche. Der tatsächliche Ligningehalt läßt sich ermitteln, wenn man von dem Gewicht des Hydrolysenrückstands die gesondert bestimmten Mengen an Fetten, Harzen und Asche abzieht. Die Notwendigkeit einer derartigen Korrektur wird jedoch bei einer Reihe von Methoden nicht beachtet, wodurch sich dann auch die abweichenden Resultate bei der Ligninbestimmung nach den verschiedenen Verfahren erklären lassen.

So findet man z.B. bei der Bestimmung des Ligningehalts durch Hydrolyse der Zellulose mit 72%iger Schwefelsäure im Sulfitzellstoff gewöhnlich 0,7 bis 0,9% Lignin. Zieht man davon das Fett und das Harz ab, so beträgt der Ligningehalt nur noch 0,25 bis 0,3%.

Das Lignin im Zellstoff beeinflußt die einzelnen Stadien des technologischen Herstellungsprozesses von Kunstfasern. Vor allem handelt es sich dabei um folgende Einflüsse:

1. Verringerung der Reaktionsfähigkeit von Zellulose sowie der Quellung und Löslichkeit in verschiedenen Agenzien. Erklären läßt sich das offenbar durch die Existenz von chemischen Bindungen zwischen den Polysaccharidmolekülen und dem Lignin, die die Bildung von Netzstrukturen hervorrufen. Je höher der Ligningehalt des Zellstoffs, um so geringer ist die Löslichkeit der Zelluloseester und um so schlechter auch die Filtrierbarkeit der erhaltenen Spinnlösungen.

2. Verzögerung des durch Luftsauerstoff in alkalischem Medium hervorgerufenen oxydativen Abbaus der Zellulosemoleküle. Hierbei ist der Einfluß des Lignins analog dem der Hemizellulosen. Baumwollinters enthalten kein Lignin, und damit kann die schnellere Vorreife der Alkalizellulose aus Linters im Vergleich zur Alkalizellulose aus Zellstoff, gleiche Bedingungen vorausgesetzt, erklärt werden.

XP-002161407

168 Methods for production of artificial fibres

...

7.314 Aldehyde and carboxyl groups.

As a result of oxidative side reactions, which happen during the cellulosic bleaching, aldehyde and carboxyl groups may occur aside of hydroxyl groups in cellulosic macromolecules. Occurrence of carboxyl groups may be also explained by forming of mixed macromolecules, containing uronic acids, formed during the biochemical synthesis.

The aldehyde groups formed in the cellulosic molecules are quantified by the copper or iod number and showing an important influence with respect to the alkaline resistance and thermo resistance of the cellulose. The more the amount of aldehyde groups, the less the resistance of cellulose against alkalines and the cellulose will be more intensively decomposed by the treatment with alkalines, especially during the mercerisation. Further, aldehyde groups effect the discoloration of cellulose at higher temperatures [14]. The higher the number of aldehyde groups, the more yellow the cellulose at higher temperatures (40 to 60 min at 110°C).

The carboxyl groups decrease the thermostability of cellulose and the fibres made thereof. Table 33 shows data [15] about the changes of the polymerisation degree of cellulose having a small content of carboxyl groups (0,004 to 0,1 %) after heating to 105°C over one hour.

Table 33 Influence of the content of carboxyl groups in cellulose of the polymerisation degree of cellulose after heating

Cellulose	Content of COOH-groups of the cellulose [%]	Decrease of the polymerisation degree after heating, based on the primary polymerisation degree [%]
Beech tree pulp I	0,004	24,8
Beech tree pulp II	0,046	4,9
Pine tree pulp I	0,004	28,3
Pine tree pulp II	0,1	4,8

In the samples marked by II the free carboxyl groups are calcium blocked by washing with water.

As shown by the data of the Table small amounts of COOH-groups cause the degregation of cellulose by heating. By blocking said groups the intensity of said thermal degregation is substantially decreased. Further, the influence of the carboxyl groups is shown in that the light resistance of the cellulose and the fibres made thereof is decreased. Thus, e.g. unbleached viscose fibres having 1 COOH-groups on 500 to 550 elementary elements, and a sample bleached with H_2O_2 (1,5 g/l) having 1 COOH-groups on 300 to 370 elements, are colored to yellow during a longer drying period.

Consequently, to obtain an increase of the light resistance and thermostability of the obtained fibres, the carboxyl groups have to be blocked in the starting pulp or the hydrate-pulp.

7.315 Lignin

...

The development of advanced cellulosic fibres

C. R. Woodings

Courtaulds plc, Coventry, UK

For the majority of the last century, commercial routes to regenerated cellulose fibres have coped with the difficulties of making a good cellulose solution by using an easy to dissolve derivative (e.g. xanthate in the case of viscose rayon) or complex (e.g. cuprammonium rayon). For the purposes of this paper, advanced cellulosic fibres are defined as those made from a process involving direct dissolution of cellulose. The first examples of such fibres have now been generically designated as lyocell fibres to distinguish them from rayons, and the first commercial lyocell fibre is Courtaulds' Tencel.

Keywords: cellulose; fibre; lyocell

Reviews of the early work on direct dissolution have been produced by Turbak[1,2]. He records the efforts to dissolve cellulose directly as a *base* using phosphoric, sulfuric and nitric 'protonic' acids, or using zinc chloride, thiocyanates, iodides and bromides as Lewis acids. With regard to cellulose acting as an *acid*, he lists sodium zincate, hydrazine, and sodium hydroxide as inorganic solvents, and quaternary ammonium hydroxides, amines, dimethylamine/dimethylsulfoxide mixtures and amine oxides as organic bases. He obtained 16% cellulose solutions in lithium chloride/dimethylacetamide systems[3] and 14% solutions in dinitrogen tetroxide/dimethylformamide systems[4]. Cuculo and Hudson[5] obtained solutions of up to 14% cellulose in an extensive study of the ammonia/ammonium thiocyanate solvent system. The dimethylsulfoxide/paraformaldehyde system, discovered by Johnson and Nicholson[6], proved capable of dissolving cellulose with a wide range of degrees of polymerization without causing degradation. However, despite early promise, the problems of developing fibre production routes using these systems have so far proved insur-mountable, with the single exception of the amine oxide route.

The cellulose-dissolving potential of the amine oxide family was first realized[7] in 1939, but it was not until 1969 that Johnson described the use of cyclic mono(N-methylamine-N-oxide) compounds (e.g. NMMO: *Figure 1*) as a solvent-size for strengthening paper[8] by partially dissolving the cellulose fibres.

Other Johnson patents[9,10] covered the preparation of cellulose solutions using NMMO and speculated about their use as dialysis membranes, food casings (sausage skins), fibres, films, paper coatings and non-woven binders. NMMO emerged as the best of the amine oxides and its commercial potential was demonstrated by Franks and Varga[11,12] of American Enka. Chanzy *et al.* at the Plant Macromoiecules Research Centre (CERMAV-CNRS) in Grenoble have studied the cellulose/NMMO system in depth[13]; a recent paper indicates that further strength increases can be obtained by adding ammonium chloride or calcium chloride to the dope[14].

Both American Enka[15] and Courtaulds set up pilot plant work in the early 1980s with the objectives of developing the fibre spinning and solvent recovery operations. To date, only Courtaulds has proceeded to full commercial scale (see next section). The Austrian viscose producer Lenzing studied various systems[16] and commenced pilot operations on an NMMO system at the end of the 1980s, but has yet to announce a commercial plant.

Work on other routes to cellulosic fibres continues, driven by a desire to identify an environmentally benign route to cellulosic fibres which will utilize the large capital investment in the xanthate route and hence cost less than a completely new fibre process.

Chen, working on a small scale at Purdue University, claims that solutions containing 10–15% cellulose in 55–80% aqueous zinc chloride can be spun into alcohol
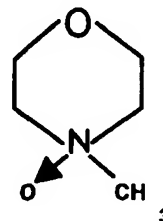
Figure 1   *N*-methyl morpholine-*N*-oxide (NMMO)

or acetone baths to give fibres with strengths of 1.5 to 2 g/den (g, grams, den, denier). However, if these fibres were strain-dried (i.e. stretched) and rewetted whilst under strain, strengths of 5.2 g/den were achieved[17].

Kamide *et al.* at Asahi have been applying the steam explosion treatment[18] to dissolving pulp to make it dissolve directly in sodium hydroxide[19]. In recent papers[20,21], they claimed to have obtained a 5% solution of steam-exploded cellulose in 9.1% NaOH at 4°C being spun into 20% H_2SO_4 at 5°C. The apparently poor fibre properties (best results being 1.8 g/den tenacity dry, with 7.3% extension) probably arise because the fibres were syringe extruded at 75 denier/filament. Asahi feel that this could be the ultimate process for large-scale production of regenerated cellulose fibres.

The Courtaulds' lyocell process

The increasing costs of reducing the environmental impact of the viscose process coupled with the increasing likelihood that the newer cellulose solvents would be capable of yielding a commercially viable fibre process led Courtaulds Research to embark on a systematic search for a new fibre process in the late 1970s. The project, codenamed 'Genesis', did not involve basic research into new solvents for cellulose so much as screening the known solvents against criteria felt to be important for the cellulosic fibre process of the future. The solvent chosen had to be recyclable at a very high level of efficiency, and hence as near to totally containable in the process as possible. It had to be safe to work with and safe in the environment in the event of any losses. It had to be able to dissolve cellulose completely without reacting with it or degrading it, and the resulting process had to be less energy-intensive than the viscose route, which had already been proven to be less energy-intensive than synthetic fibres in an independent study. It was especially important to choose a system which, like the melt-spun synthetic fibres system, would not require costly gaseous or liquid effluent treatment systems. Finally, the process had to be capable of making good textile fibres to maintain, or even extend, the cellulosic fibre share of the global market, against fierce competition from melt-spun synthetic fibres based on cheap but non-renewable oil reserves.

By 1980, NMMO had been shown to be the best solvent, provided well-known difficulties associated with its thermal stability could be avoided by appropriate chemical engineering. Filaments obtained from the first single-hole extrusion experiments had promising properties, so Courtaulds committed the resources (1982) to build the first small pilot plant to test the feasibility of overcoming the solvent-handling and recovery problems which had prevented earlier commercial exploitation. This system, capable of making up to 100 kg/week of fibre, met its objectives and allowed the first serious end-use development to begin. Scale-up to a 1000 kg/week pilot line was possible in 1984, and a 25 000 kg/week semi-commercial line was commissioned in 1988 to allow a thorough test of the engineering and end-use development aspects.

Comparisons of lyocell with viscose in both laboratory and test markets proved that the fibres were sufficiently

different to deserve separate marketing strategies. Lyocell was:

- stronger than any other cellulosic fibres, especially when wet
- easy to process into yarns and fabrics alone or in blends
- easy to blend (unique fibre presentation)
- easy to spin to fine count yarns
- very stable in washing and drying
- thermally stable
- easy to dye to deep vibrant colours
- capable of taking the latest finishing techniques to give unique drape
- comfortable to wear

As a 1.5 denier fibre, it could be spun into yarns with a better strength conversion factor than other cellulosic fibres, allowing rotor-spun lyocell to out-perform ring-spun cotton or modal viscose. Fabrics could be made at high efficiency, and proved to have the anticipated tear and tensile advantages over other cellulosic fibres. Direct, reactive or vat dyes could be used, and easy-care properties could be achieved with less resin finish than normal. Lyocell could therefore be marketed as a new premium-quality clothing cellulosic fibre and not simply as a long-term replacement for viscose.

The Courtaulds semi-commercial production system is illustrated in *Figure 2*. Dissolving grade woodpulp is mixed into a paste with NMMO and passes through a high-temperature dissolving unit to yield a clear viscous solution. This is filtered and spun into dilute NMMO, whereupon the cellulose fibres precipitate. These are washed and dried, and finally baled as staple or tow products as required by the market. The spin-bath and wash liquors are passed to solvent recovery systems which concentrate the NMMO to the level required for re-use in dissolution.

As mentioned above, the new fibre has physical properties (*Table 1*) which are sufficiently different from regular rayon to allow an initial market development strategy which does not erode the position of the traditional viscose fibre. The unique strength, texture and
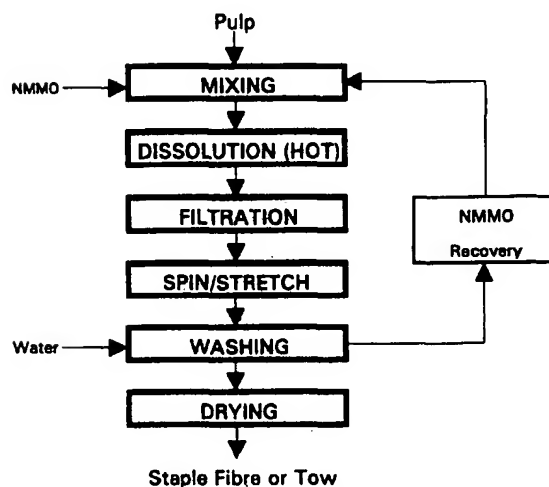

Pulp

NMMO → MIXING

DISSOLUTION (HOT)

FILTRATION

SPIN/STRETCH

Water → WASHING

DRYING

NMMO Recovery

Staple Fibre or Tow

Figure 2 Direct dissolution: Courtaulds' lyocell

Table 1 The properties of selected commercial rayon fibres

Property	Cuprammonium	Regular rayon	Improved rayon	Modal	Polynosic	'Y'-shaped rayon[a]	Solvent-spun rayon[b]
Fibre cross-section							
Dry tenacity (cN/tex)	15–20	20–24	24–30	34–36	40–45	18–22	40–44
Extensibility at break % (dry)	7–23	20–25	20–25	13–15	8–12	17–22	14–16
Wet tenacity (cN/tex)	9–12	10–15	12–16	19–21	30–40	9–12	34–38
Extensibility at break % (wet)	16–43	25–30	25–35	13–15	10–15	23–30	16–18
Water imbibition (%)	100	90–100	90–100	75–80	55–70	100–110	65–70
Cellulose D.P.	450–550	250–350	250–350	300–500	550–700	250–350	550–600
Initial wet modulus (@ 5%)	30–50	40–50	40–50	100–120	140–180	35–45	250–270

[a]The 'Y'-shaped rayon data are based on Courtaulds' Galaxy fibre
[b]The solvent-spun rayon data are based on Courtaulds' Tencel fibre

coloration potential of the fibre enable it to command premium prices for upmarket men's and ladies' outwear. The existing process will also be capable of meeting the needs of the industrial, non-woven and speciality paper markets as these end-uses are developed. Several studies of its performance in non-woven fabrics show it capable of yielding fabric strengths between two and three times higher than hitherto possible with regenerated cellulosic fibres[22,23]. It appears particularly suitable for the latest hydroentanglement systems[24] where its basic strength and ability to develop a micro-fibre surface under the action of high-pressure water jets enable it to be made into very strong non-woven fabrics with textile-like properties.

Continuous operation of the 25 000 kg/week semi-commercial line provided the necessary confidence in both process and market to justify full commercial operation. An 18 000 tonne/year line was therefore designed and built in Mobile (Alabama, USA) in 1991/1992. Since its commissioning in May 1992, this plant has approached its target productivity and quality, and is now supplying fibre to several major clothing markets. It is set up to be capable of making the range of fibre deniers and lengths required for premium-quality textiles and non-woven fabrics. In the summer of 1995, the capacity of the Mobile plant was more than doubled. Plans for a second plant in Europe are already advanced, and the options for a third plant in the Far East are being investigated.

Environmental issues

Fibre production

Cellulose is the natural polymer which makes up the living cells of all vegetation. It is the material at the centre of the carbon cycle, the most abundant and renewable biopolymer on the planet. Rayon fibre producers have converted it into fine textile fibres used for almost a century but rayon remains unique among the mass-produced manmade fibres because it is the only one to use the natural polymer directly. Cellulosic fibres therefore have much to recommend them provided that the processes used to make them have minimal environmental impact.

The solvent-spun process, as currently designed, will use the same sources of pulp (at slightly higher levels of efficiency) as the viscose process. Alternative pulping sequences which eliminate all chlorine compounds from the process are being investigated for use in both viscose and solvent systems.

Amine oxide solvent. N-methylmorpholine N-oxide (NMMO) is the solvent used. It is manufactured by methylation and oxidation of morpholine, which comes from a reaction between diethylene glycol and ammonia. This is the only major chemical used in the solvent-spun process, and its consumption is reduced to the absolute minimum by recycling, which is made possible by solvent recovery.

Energy. Early attempts to assess the total energy required to make baled staple fibre from naturally occurring raw materials (wood in the case of cellulosic fibres and oil in the case of synthetic fibres) used differing approaches and were insufficiently rigorous to allow hard conclusions to be drawn. In general, the authors[25-30] subdivided the fibre production sequence into monomer making, polymer making and fibre production, and, while a variety of fibres are covered, only viscose rayon and polyester are mentioned in all of these publications. Tonnes of fuel-oil-equivalent per tonne of fibre (TFOE/T) were the most popular units, with rayon requiring from 1.7 to 2.4 TFOE/T and polyester requiring 2.6 to 4.2 TFOE/T.

The studies all concluded that rayon required less energy to make than polyester, but there was little agreement on the magnitude of the difference. The wet-spun cellulosic fibres required more energy than

melt-spun polyester for the fibre-making step, but they had no monomer energy requirement. The 'polymerization' requirement was therefore minimal. In the case of the 1.7 TFOE/T figure for rayon, full credit was being given for the fact that the pulp mill energy needs were renewable and not dependent on fossil fuels. Pulp could be fed directly into the viscose process without incurring any transport or drying cost, and the pulp mill could be driven entirely by energy obtained from burning the parts of the tree which were not needed in the final product. This 'free' and renewable energy was not counted.

From an energy viewpoint, the solvent route to cellulosic fibres is identical to the viscose route up to the point where the cellulose enters the solvent. The energy requirement for the non-cellulosic raw materials is significantly lower in the case of the solvent route, but the solvent route requires similar energy levels for dope handling, spinning, washing and recycling. The lower water imbibition of the solvent fibre (65% versus 95%) yields savings in fibre drying and of course in any subsequent washing and drying operations.

Overall, the solvent route shows a useful economy in this important resource when compared with viscose production on the same scale.

Fossil reserves. Renewable resources will become increasingly important as the planet's stocks of fossilized reserves are depleted and as governments realize that biomass can provide a truly sustainable, cost-effective source of energy and materials. As indicated above, the recycling rate is so high that solvent usage is kept down to a few kg per tonne of fibre, and hence fossil reserve dependence is minimal.

Gaseous effluents. The solvent process involves direct dissolution of cellulose in a liquid which is recycled very efficiently. There are no chemical reactions and no by-products of the sort which are unavoidable in the regeneration of cellulose from the viscose route.

The solvent process produces very little atmospheric emission. Traces of volatile organic compounds associated with the solvent and the soft finish leave the plant in the normal course of ventilation.

Liquid effluents. The solvent route uses much less water than the viscose process and the process effluent needs significantly less treatment.

Fibre disposal

Cellulosic fibres, like the vegetation from which they arise, can become food for micro-organisms and higher life forms: in other words, they biodegrade. In complete biodegradation or incineration, the final breakdown products are carbon dioxide and water; these disposal methods simply recycle the cellulose to the atmospheric components from which it was made.

It is also possible to liberate and use some of the 'free' solar energy which powered the manufacture of sugars and cellulose during photosynthesis. This can be achieved by burning or by anaerobic digestion. Slow anaerobic biodegradation occurs in all landfill sites dealing with municipal solid waste. This process generates methane from cellulose, which can be burnt to drive gas turbines. If future landfills are lined and operated with moisture

addition and leachate recycling, then energy generation and the return of landfill sites to normal use can be accelerated[31].

Commercial issues

In the last ten years, viscose-based staple fibres have, like the cuprammonium and viscose filament yarns a decade earlier, ceased to be commodities. They have been repositioned in the market from low-cost textile fibres which were used in a myriad of applications regardless of suitability, to premium-priced fashion fibres delivering comfort, texture and attractive colours in ways which are hard to achieve with synthetic fibres. They are still widely used in blends with polyester and cotton to add value, whereas a decade ago they would have been added to reduce costs.

Such repositioning inevitably means reduced production volume, and, for the first time this century, production in the last decade has been below that a decade earlier (*Figure 3*). Most capacity reductions have been in North America and in Europe, especially the Eastern part. This has been offset in part by capacity increases in the Far East. Rayon is no longer a major component of carpets, and has lost the disposable diaper (nappy) coverstock business to cheaper and more easily processed polypropylene. However, it has gained a share in health and hygiene products and is now a major component of tampons worldwide.

The lyocell fibres now being introduced have the capability to halt the overall decline in manmade cellulosic fibres' share of the world market. In clothing textiles, Courtaulds' Tencel™ had early successes in market sectors which were previously closed to the other manmade cellulosic fibres. The combination of the unique fibre properties with novel fabric and garment finishing techniques yielded highly desirable garment aesthetics. These aesthetics have proved attractive in garments as diverse as denim and underwear.

In non-woven fabrics, lyocell's inherent strength and 'bondability' have led to a variety of new applications which were not possible with viscose rayon. In hydro-entanglement, one of the fastest growing sectors of the non-woven industry, the use of Courtaulds' lyocell is now showing several advantages over other cellulosic fibres. Compared with viscose or cotton, it allows the
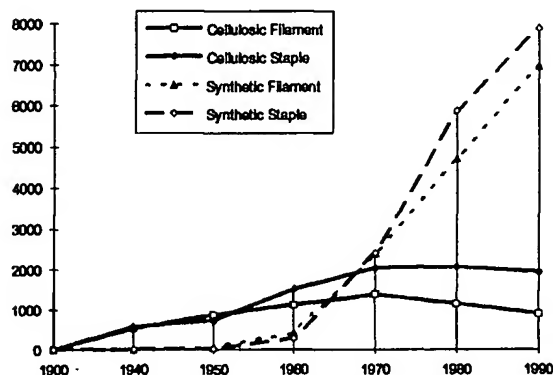

Figure 3 World manmade fibre production: 1900–1990

manufacture of a wider range of basis weights, with higher strengths, better appearance and improved dry and wet textures. At high bonding pressures, it has enabled the production of non-woven fabrics which are stronger than the same weight of woven cotton. When fibrillated by refining or very-high-pressure hydroentanglement, the microfibres generated may be used in leather- or suede-like materials, efficient filters, or even durable papers.

Conclusion

Rayon fibres, made for a century by the direct conversion of abundant vegetable matter, have always had much to recommend them in textiles compared with synthetic fibres made from fossil fuels. The renewability of their main raw material, their overall energy efficiency, their lack of dependence on fossil fuels, their long history of safe use in hygiene applications, and their easy disposal and natural recyclability make them strong contenders for tomorrow's textile industry also.

The new solvent route to rayon reinforces these inherent strengths by using a modern fibre production system, which, being physical rather than chemical, reduces environmental impact to a minimum. The Tencel investment, coupled with continuous improvement of the traditional route, gives us what we believe is a winning approach to textile industry fibre supply for some time to come.

References

1 Turbak, A.F. *et al.* 'A Critical Review of Cellulose Solvent Systems', ACS Symposium Series 58, American Chemical Society, 1977
2 Turbak, A.F. 'Proceedings of the 1983 International Dissolving and Speciality Pulps Conference', 1983, p 105
3 Turbak, A.F., El-Kafrawy, A., Snyder F.W. Jr and Auerbach, A.B. US Patent 4 302 252 (24 November 1981), to International Telephone and Telegraph Corp
4 Turbak, A.F. and Hammer, R.B. US Patent 4 056 675 (1 November 1977), to International Telephone and Telegraph Corp
5 Cuculo, J.A. and Hudson, S.M. US Patent 4 367 191 (4 January 1983), to Research Corporation
6 Johnson, D.C. and Nicholson, M.D. US Patent 4 097 666 (27 June 1978), to the Institute of Paper Chemistry
7 Graenacher, C. and Sallman, R. US Patent 2 179 181 (7 November 1939), to Society of Chemical Industry in Basle
8 Johnson, D.L. US Patent 3 447 956 (3 June 1969), to Eastman Kodak Company
9 Johnson, D.L. US Patent 3 447 939 (3 June 1969), to Eastman Kodak Company
10 Johnson, D.L. US Patent 3 508 941 (28 April 1970), to Eastman Kodak Company
11 Franks, N.E. and Varga, J.K. US Patent 4 145 532 (20 March 1979), to Akzona Inc
12 Franks, N.E. and Varga, J.K. US Patent 4 196 282 (1 April 1980), to Akzona Inc
13 Chanzy, H., Peguy, A., Chaunis, S. and Manzie, P. *J. Polym. Sci. Polym. Phys. Educ.* 1980, **18**, 1137–1144
14 Chanzy, H., Paillet, M. and Hagege, R. *Polymer* 1990, 31
15 Armstrong, R.N. *et al.* 'Proceedings of the 5th International Dissolving Pulps Conference', 1980
16 Lenz, L. *J. Appl. Polym. Sci.* 1988, **35**, 1987–2000
17 Chen, L.F. US Patent 4 999 149 (12 March 1991), to Purdue Research Foundation
18 Watanabe, T. *et al.* Preprint for the 20th Annual Meeting of Polymer Science, Japan, 1971, p 427
19 Kamide, K. *et al. Br. Polym. J.* 1990, **22**, 73–83, 121–128, 201–212
20 Kamide, K. and Yamashiki, T. 'Cellulose Sources and Exploitation', chapter 24, Ellis Horwood Ltd, Chichester, 1990
21 Kamide, K. *et al. J. Appl. Polym. Sci.* 1992, **44**, 691–698
22 Smith, D.A., Williams, S.D.J. and Woodings, C.R. 'Proceedings of the EDANA Index 87 Symposium', 1987
23 Cole, D. and Woodings, C.R. 'Proceedings of the EDANA Index 90 Symposium', 1990
24 Woodings, C.R. 'Proceedings of the IMPACT 89 Nonwovens Conference', Miller Freeman Publications, 1989
25 Woodhead; ICI; 'International TNO Conference', 1976
26 Lane, M. and McCombes, J. *Textile Manufacturer* 1979, 1,
27 Kogler, F. 'Proceedings of the EDANA AGM', Munich, 1980
28 Armstrong, R. 'Proceedings of the EDANA AGM', Munich, 1980
29 Marini, I. and Six, W. 'Proceedings of the EDANA Nonwovens Symposium', Milan, 1985
30 Frith, W.C. 'Energy Balance of Man-Made Fibre Production', Committee Internationale Rayon et Fibres Synthetiques, 1980
31 Pohland, F. and Sratakis, M. 'Proceedings of Insight 91', Charleston, VA, USA, October 1991

Crystallinity changes in lyocell and viscose-type fibres by caustic treatment

X. Colom *, F. Carrillo

Departament d'Enginyeria Química, Universitat Politècnica de Catalunya, Colom 1, 08222 Terrassa, Spain

Received 4 December 2001; received in revised form 1 April 2002; accepted 17 April 2002

Abstract

One of the most important treatments performed on cellulosic fibres to improve properties such as dimensional stability, tensile strength and lustre, is mercerisation. The aim of this work was to study the crystallinity, accessibility and unit cell structure changes occurring in three types of regenerated cellulose fibres (lyocell, modal and viscose) that were mercerised with caustic soda solutions of different concentrations. Differences were observed between the behaviour of the viscose type fibres (viscose and modal) and that of the lyocell fibres. For the viscose type fibres, the proportion of crystalline regions increased at low alkali concentrations, while for lyocell fibres a decrease in crystallinity was observed. In all three fibres there was a transformation from cellulose II to amorphous cellulose. While for lyocell the transformation was partial, the modal and in particular the viscose fibres showed a complete transformation, and the swelling agent caused the fibre to dissolve at high caustic concentrations.
© 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Lyocell; Viscose-type fibres; Infrared (IR) spectroscopy; Crystallinity; Caustic treatment

1. Introduction

Over the years, much effort has been spent on finding an artificial silk and several different cellulose derivatives have been examined. However, only two (acetate and xanthate ester) are of commercial importance today. Both have been used for many decades in the regeneration of wood cellulose to form fibres and films. Recently, however, there has been intensive research into the commercial regeneration of cellulose due to the environmental problems associated with the xanthate process [1]. Among the many aqueous and non-aqueous cellulose solvent systems reported in the past three decades, only *N*-methyl-morpholine-*N*-oxide (NMMO) has been successfully used in the production of regenerated cellulose textile fibres [2]. The fibres regenerated from NMMO solutions, known with the generic name of lyocell [3],

have higher crystallinity and amorphous orientation. This yields cellulose fibres with higher wet strength than those produced using the earlier technologies [4].

The swelling of regenerated cellulose in alkali solutions has been applied industrially for many years. This process causes changes in the crystallinity, accessibility, unit cell structure, and orientation of fibrils in cellulosic fibres. The extent to which sodium hydroxide solutions change these properties depends on factors such as the concentration of the sodium hydroxide solution, the temperature, the degree of polymerisation, the source of the cellulose, the physical state of the cellulose (i.e., fibre, yarn or fabric), and the degree of tension employed to restrict or promote fibre shrinkage and swelling. These variables have been effectively controlled for the mercerisation of cotton along with other celluloses and blends of synthetic fibres and cellulose in order to improve or optimise one or more of the following properties: dimensional stability, affinity for dyes, tensile strength, higher add-on of finishing agents, lustre and fabric smoothness [5].

* Corresponding author. Fax: +34-93-739-8225.
E-mail address: colomf@eq.upc.es (X. Colom).

In cellulose samples that have been subjected to a mercerisation process, the relative amounts of crystalline and amorphous regions and the amounts of cellulose I and cellulose II vary simultaneously. In order to follow this process, the infrared ratios proposed by O'Connor et al. [6,7] were used. They suggested that the regions 1372–1375 cm⁻¹ (CH-bending) and 2900 cm⁻¹ (CH-stretching) to be the most suitable for indicating crystallinity changes. This is a good method for studying changes in the microstructure, for example, when treating cellulose with sodium hydroxide, where there should be a decrease in the crystalline index or conversion of the cellulose I structure to cellulose II and amorphous structure.

The aim of this study was to compare the changes in the supermolecular structure and the accessibility of the three different regenerated cellulose fibres (viscose and modal, obtained from the xanthate process, and lyocell, based on the solvent NMMO process) which were treated with sodium hydroxide. The purpose of this study was to better understand fibre microstructure behaviour and to find ways to further improve its properties.

2. Experimental

2.1. Materials

Lyocell, viscose and modal staple fibres of 1.7 dtex, supplied by Lenzing Lyocell were used.

2.2. Caustic soda treatment

The samples were washed in a sodium carbonate solution (2 g/l) for 30 min at 30 °C. They were then wrung out, rinsed with distilled water and dried at 105 °C for 2 h. Two and a half grams of the dried fibres were treated for 30 min with different NaOH solutions at 20 °C, with a bath ratio of 11:1. Caustic concentrations in the bath were 6.2, 12.4, 16.7, 17.7, 18.0, 21.4, 24.0, 30.0, 40.0 and 50.0 g NaOH/100 ml respectively. When the treatment period was over, the various fibres were wrung out, rinsed and air-dried at 40 °C.

2.3. Moisture regain

The moisture regain measurements, taken from the dry side, were obtained after the desiccation (over P_2O_5) of the samples at room temperature over three days, followed by conditioning for one week over a saturated magnesium acetate solution at 20 °C (RH: 65%) [8].

2.4. Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) spectra were obtained by means of a spectrometer Nicolet Avatar 320 with CsI optics. Samples of the finely divided material (1.5 mg) were ground and dispersed in a matrix of KBr (100 mg). A pellet was then formed by compression at 167 MPa. The sample collection was obtained using 100 scans and a resolution of 2 cm⁻¹.

3. Results and discussion

3.1. Spectral study of regenerated cellulose fibres

Previous work demonstrates, by means of various methods (X-rays, IR), that the cellulose fibres are made up of a mixture of three components, these being crystalline cellulose I, crystalline cellulose II and amorphous cellulose [9]. The differences observed in the mechanical and chemical behaviour of different fibres lead us to believe that these fibres, which have similar chemical compositions, differ in the percentage composition of each component, thus allowing specific conformations with some structural differences.

The infrared spectra in the 1660–870 cm⁻¹ region of the three regenerated cellulose fibres studied are shown in Fig. 1. This region contains the largest number of spectral differences, which allows for the identification of the structural changes in the cellulosic fibres. Table 1 shows the most significant bands that were studied and analysed, and their corresponding assignments.

The absorption bands indicated in Fig. 1 are assigned mainly to crystalline cellulose II and amorphous cellulose. The 1420 cm⁻¹ band is characteristic of both cellulose II and the amorphous cellulose. If a cellulose fibre
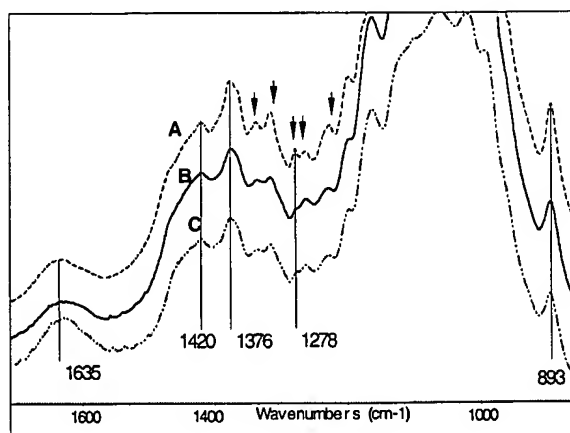

Fig. 1. Spectral area of 1660–870 cm⁻¹ corresponding to the fibres such as: (A) lyocell, (B) modal and (C) viscose.

Table 1
Characteristic absorption bands of regenerated cellulose fibres

Wavenumber (cm^{-1})	Assignment
1420	δ CH$_2$ symmetric bending
1376	C–H bending
1336	C–OH in plane bending
1316	CH$_2$ wagging
1278	C–H bending
1235	C–OH in plane bending
1227	C–OH in plane bending
893	γ (COC) in plane, symmetric stretching

has a significant amount of crystalline cellulose I, this band moves toward 1430 cm^{-1} and the amounts of cellulose II and amorphous cellulose decreases. The absence of an appreciable band at 1430 and at 1111 cm^{-1} indicates that crystalline cellulose I is practically non-existent in the regenerated cellulose fibres.

Bands 1336 and 1316 cm^{-1} (marked by arrows in Fig. 1) show significant differences in their absorbances. The 1316 cm^{-1} band assigned to both crystalline celluloses (Cel I and Cel II) is much more intense in the lyocell fibre than in the other two fibres.

The absorption bands at 1336, 1316, 1278, 1262, 1234 and 1227 cm^{-1} in regenerated cellulose fibres are due to differences in their structural composition and relative amount of each constituent. Nelson et al. [6] found that the bands 1336, 1316, 1278 and 1227 cm^{-1} showed the greatest differences between the crystalline cellulose II and the amorphous cellulose, and Kondo et al. [10] demonstrate that these bands were not characteristic of the amorphous area. As can be seen, the absorption bands at 1336, 1316, 1278 and 1227 cm^{-1} show peaks of greater intensity for the lyocell fibres. This shows that the ratio of crystalline cellulose II to amorphous cellulose in lyocell fibres is greater than that of modal and viscose.

Table 2 shows the infrared crystallinity index results obtained for lyocell, viscose and modal fibres. These indexes have been calculated by the infrared ratios

proposed by Nelson and O'Connor [6,7], a_{1376}/a_{2902} (total crystalline index (TCI)) and a_{1420}/a_{893} (lateral order index (LOI)), and the doublet a_{1278}/a_{1263} proposed by Carrillo–Colom in previous work [11]. It can be seen that these infrared ratios produce different values which represent spectral differences, due to the different structural conformation of regenerated cellulose fibres, which we will discuss later. Lyocell fibres have a higher crystallinity than viscose-type fibres. This is confirmed by the respective FTIR 1420/893 and 1278/1263 ratios, which show lower values for lyocell samples.

3.2. Comparative study of cellulose fibres upon mercerisation treatment

In the FTIR spectral region studied, significant differences in intensity and shape could be observed between the different samples after mercerisation. Viscose was the type most affected by this treatment, and reached dissolution at caustic soda concentrations higher than 16.7 g/100 ml. Moreover, after the treatment we could often observe a partial dissolution. The same observations could be made for the modal fibres, but the extent of the effects was less. For the lyocell sample, no physical differences or transformations were detected after the treatment.

The 1400–1200 cm^{-1} spectral region of a series of mercerised cellulose fibres is shown in Fig. 2(a)–(c). This region includes the bands 1376, 1336, 1316, 1278, 1265, 1234 and 1227 cm^{-1}, assigned previously in Table 1. The intensity and shape evolution of these infrared absorbance bands define the structural changes caused by the caustic treatment.

The results of the infrared crystallinity ratios obtained for each fibre, as a function of different concentration of caustic treatment, are shown in Table 2.

From the tabulated values it can be noted that the TCI shows no significant changes for any of the samples. This infrared ratio, defined and contrasted by Nelson et al. by means of X-ray diffraction, indicated that the mercerisation process of the cellulose substrates without

Table 2
Infrared crystallinity indexes data on lyocell, modal and viscose, after caustic treatments

g/100 ml (NaOH)	1376/2902 (TCI)			1420/893 (LOI)*			1278/1263 (CCI)		
	Lyocell	Viscose	Modal	Lyocell	Viscose	Modal	Lyocell	Viscose	Modal
0	0.742	0.68	0.73	0.341 (80%)	0.54 (41%)	0.52 (49%)	0.66	1.17	1.02
6.2	0.715	0.68	0.72	0.387 (72%)	0.36 (77%)	0.35 (78%)	0.81	0.6	0.44
12.4	0.710	0.69	0.72	0.409 (68%)	0.37 (76%)	0.45 (69%)	0.86	0.65	0.90
14.5	0.748	0.64	0.74	0.421 (65%)	0.42 (65%)	0.49 (50%)	0.9	0.81	0.94
16.7	0.725	0.66	0.73	0.436 (62%)	0.45 (69%)	0.50 (48%)	1.09	1.08	1.07
18.0	0.761	–	–	0.472 (54%)	–	–	1.31	1.13	1.10
24.0	0.732	–	–	0.581 (30%)	–	–	1.18	1.19	1.37

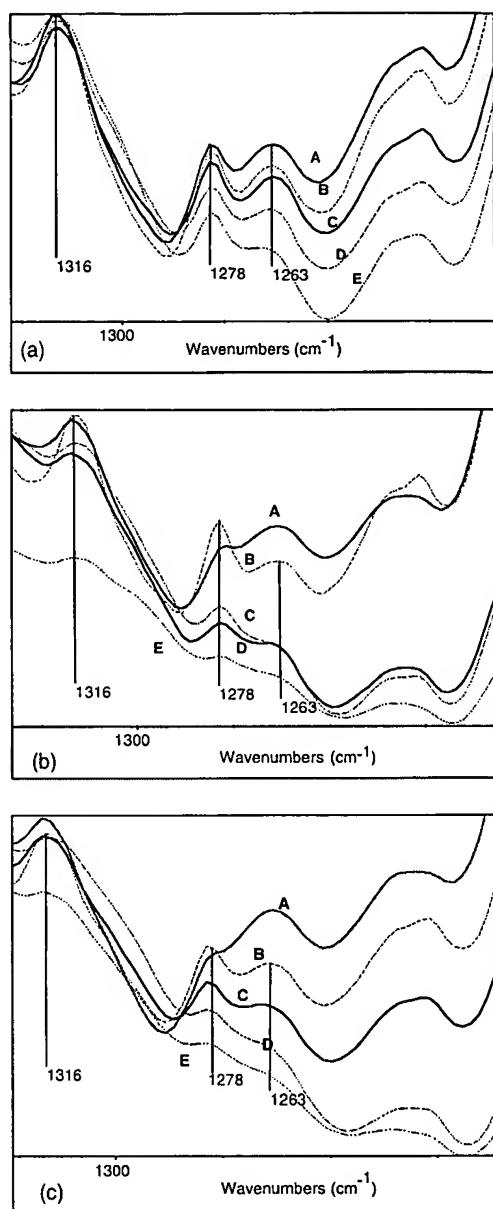*The values of the degree of crystallinity [14] are in parentheses.

Fig. 2. Spectral area corresponding to: (a) lyocell, (b) modal, and (c) viscose fibres, illustrating the changes caused by the caustic treatments. (A: 0 g NaOH, B: 6.2 g NaOH, C: 12.4 g NaOH, D: 18.0 g NaOH, E: 24.0 g NaOH).

crystalline cellulose I content cannot be considered a reliable indicator of the structural changes occurring in the alkaline degradation process. Nevertheless, previous studies [12,13] of substrates with a high crystalline cellulose I content demonstrate that this ratio is useful to follow structural changes during caustic treatments.

However, the LOI and the 1278/1264 ratio bands allow us to follow structural changes caused by the mer-

cerisation stage. Both ratios were observed to have similar behaviour, although it should be pointed out that the 1278/1264 ratio was more sensitive in the case of the LOI.

Significant differences in behaviour can be discerned between the lyocell and the viscose type fibres. The lyocell fibre crystallinity decreases with increases in the concentration of the sodium hydroxide solution. Using the correlation proposed by O'Connor et al. to obtain the degree of crystallinity, by means of X-ray diffraction, according to Wakelin [14], it is evident from the LOI results that there is a decrease in the degree of crystallinity (in parentheses) of these fibres from 0.34 (80%) to 0.58 (30%).

Modal and viscose fibres show a completely different evolution of these infrared ratios. The initial degree of crystalline cellulose II is lower than that of lyocell: 41% for viscose and 49% for modal fibres. As is shown in Table 2, the LOI ratios reveal that there is initially a noticeable decrease, from 0.54 to 0.36 and 0.52 to 0.35 for viscose and modal respectively. This corresponds to an increase in crystallinity from 41% to 77% and 49% to 78% for the viscose and modal samples. Caustic concentrations of up to 12.4 g NaOH/100 ml produce a decrease in crystallinity until there is total dissolution at high concentrations of sodium hydroxide. The same behaviour is observed for the 1278/1264 relation bands. With this kind of viscose type fibre, the crystallinity of the untreated samples is initially below that of the pre-treated fibres, and there is evidence of a certain amount of recrystallization under alkaline conditions. The increase in crystallinity of viscose and modal fibres after treatment with sodium hydroxide has been observed by Sreenivasan et al. [15] and Rusznák et al. [16]. These authors explained the recrystallization as a mobilisation of the cellulose molecules by cleavage of hydrogen bonds. The later progressive decrease in the degree of crystallinity, at high caustic concentration, by the transformation of the crystalline structure from cellulose II to amorphous cellulose, disproves the possibility that this increase might be caused mainly by dissolution and removal of separate short chain fractions from the bulk fibrous system.

As this initial increase in crystallinity is not present in lyocell fibres, it could be said that modal and viscose fibres are made up of cellulose II, amorphous cellulose and a region of transitory structure caused by the collapse of the high-molecular chains that occurs during spinning process. The alkali treatment produces a structural relaxation of these collapsed cellulose chains, which facilitates a new reorientation towards the crystalline structure of cellulose II.

The difference between solvent spun lyocell and the viscose type fibres is a result of the spinning process. In the old viscose processes, the dissolved macromolecules are completely disordered. During fibre formation not

only must they be oriented in order to form the crystallites, but decomposition must also take place in order to regenerate the cellulose derivative. With the dissolution of the new organic solvent cellulose, no decomposition is required and the dissolved macromolecules are already somewhat oriented before fibre formation. Orientation and structure formation is thus easier.

The viscose fibre spectrum obtained at high concentrations of sodium hydroxide (about 18 g/100 ml H_2O), shows that all the characteristic bands of the crystalline structure of cellulose II disappear, indicating the transformation to an amorphous structure. Concentrations up to 18 g NaOH/100 ml H_2O cause the dissolution of viscose forming a gel. For modal fibre the total transformation of cellulose II to amorphous cellulose takes place from 24 g NaOH/100 ml and it becomes a gel at sodium hydroxide concentrations higher than 30 g NaOH/100 ml. However, lyocell fibres retain part of the cellulose II formation at concentrations higher than 24 g NaOH/100 ml. This indicates that the structure of the lyocell fibre is more compact and prevents the distortion of the macromolecules by the penetration of swelling agents, thus providing its resistance to high caustic concentrations.

3.3. Analysis of the moisture regain

One can estimate the extent of less ordered regions in a fibre by evaluating moisture regain. Cellulose fibres with greater amorphous content absorb a greater quantity of water. Fig. 3 shows the moisture regain data evolution for the untreated samples and the samples mercerised by sodium hydroxide solutions. The percentage of moisture absorbed by the untreated fibres is less for the lyocell (12%) than for viscose type fibres (15%). This is as a result of the greater degree of crystallinity of the lyocell.

The changes in moisture regain for viscose type fibres and lyocell fibres is different. The lyocell fibres show increased and sustained moisture regain between 12% and 18%. The modal and viscose fibres, however, show similar behaviours, although they follow a significantly different development. At first the fibres have a constant value of moisture regain, even showing a decrease up to concentrations of 8 g NaOH/100 ml. At higher concentrations, the moisture regain increases up to a maximum value of 23% (18 g NaOH/100 ml) for viscose and 21.5% (21.5 g NaOH/100 ml) for modal. After these maximum values, a decrease follows due to the total dissolution of viscose and partial dissolution of modal samples.

These results support the observations from FTIR experiments. Lyocell fibres retain a smaller quantity of water because of their structure: high crystallinity and
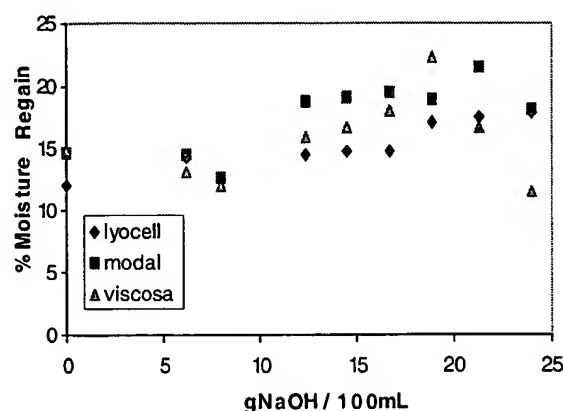

Fig. 3. Moisture regain changes for the different regenerated cellulose samples.

orientation are less affected by the swelling agent. However, the modal and mainly viscose fibres are more affected by the mercerisation process, reaching total dissolution at higher sodium hydroxide concentrations. The decreasing moisture regain value at low caustic concentrations for viscose type fibres indicates the initial recrystallization stage.

4. Conclusions

Like viscose type fibres, lyocell fibres consist of crystalline cellulose II and amorphous cellulose. Solvent spun lyocell fibres have a higher degree of crystallinity (80%) than the 49% and 41% crystallinity in the modal and viscose fibres respectively.

It has been observed that during the mercerisation treatment the viscose type fibres are more affected to the degradation caused by the transformation of crystalline cellulose II to amorphous cellulose, to the point of total dissolution at high caustic concentrations for modal and viscose. For lyocell fibres, this transformation is partial and dissolution at high concentration does not occur. This can be explained by the orientation and high crystallinity of the lyocell macromolecules. This property inhibits the effect of swelling agents and limits degradation.

The spinning process involved in viscose type fibres produces a transitory structure caused by the collapse of the high-molecular chains that has not been observed in lyocell. As a consequence, the treatment induces a relaxed structure in these collapsed cellulose chains at low alkali concentration, which facilitates reorientation towards the crystalline structure of cellulose II. This produces an increase in the crystallinity, as indicated by the

1420/893 (LOI) ratio along with the 1278/1263 ratio, as proposed by Carrillo and Colom.

The moisture regain results support the FTIR conclusions.

Acknowledgements

References

[1] Chegolya AS, Grinshpan DD, Burd EZ. Text Res J 1989;59:501–6.

[2] Bochek AM, Petropavlovsky GA, Yakimansky AV. Cellulose and cellulose derivates: physico-chemical aspects and industrial applications. Abington Hall, Abington: Woodhead Publishing Limited; 1995.

[3] ISO 2076, Textiles—Man-made Fibers—Generic names 1995-12-12, Reference number ISO/TC 38/SC N 1631.

[4] Lenz J, Shurz J, Wrentschur E. J Appl Polym Sci 1998;35: 1988–2000.

[5] Kennedy J, Phillips G, Willians P. Allomorphs of cellulose and other polysaccharides. Cambridge: Woodhead Publishing Limited; 1996.

[6] Nelson ML, O'Connor RT. J Appl Polym Sci 1964;8:1311–24.

[7] Nelson ML, O'Connor RT. J Appl Polym Sci 1964;8:1325–41.

[8] Segal L, Creely JJ, Martin AE, Conrad CM. Text Res J 1959;29:786–94.

[9] Kroschwitz J, Howe-Grant M. Encyclopedia of chemical technology. New York: Wiley-Interscience Publication; 1993.

[10] Kondo T, Sawatari C. Polymer 1996;37(3):393–9.

[11] Colom X, Carrillo F, Moratalla G, Nogués F. In: International Textile Congress, Conference Proceedings, vol I, Terrassa, Spain, 2001. p. 29–38.

[12] Ferrús R, Pagès P. Cell Chem Technol 1989;11:633–7.

[13] Nogués F, Carrillo F, Colom X. AFINIDAD 2002; 498(59):104–10.

[14] Wakelin JH, Virgin HS, Crystal E. J Appl Phys 1957;30: 1654.

[15] Sreenivasan S, Krishna Iyer KR, Chidambareswaran PK, Patil NB. Text Res J 1988;31:299.

[16] Rusznák I, Schenker B, Bodor G. Cell Chem Tech 1989;23: 401–14.